

11 9 APR 2005



PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C11D 3/50, 17/00, 3/12, A61K 7/46		A1	(11) International Publication Number: WO 94/28107
			(43) International Publication Date: 8 December 1994 (08.12.94)
(21) International Application Number: PCT/US94/06050 (22) International Filing Date: 31 May 1994 (31.05.94) (30) Priority Data: 08/071,124 2 June 1993 (02.06.93) US (71) Applicant: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors: PAN, Robert, Ya-Lin; 5750 Samstone Court, Cincinnati, OH 45242 (US). You, Jing-Feng; 5460 Fawn- view Court, West Chester, OH 45069 (US). CARAVA- JAL, Gregory, Stephen; 1586 Gelhot, #219, Fairfield, OH 45014 (US). GRAVES, Sharon, Anne; 19188 Par Drive, Lawrenceburg, OH 47025 (US). MUELLER, William, Richard; 2432 Swales Drive, Lawrenceburg, OH 47025 (US). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>	
(54) Title: PERFUME DELIVERY SYSTEM COMPRISING ZEOLITES			
(57) Abstract			
<p>Granular detergent compositions comprise conventional ingredients and a perfume delivery system which comprises Type X or Type Y Zeolites having a perfume releasably adsorbed within their pores, and a barrier matrix comprising a fluid polyol or diol which is insoluble with the perfume and a solid polyol containing more than three hydroxyl moieties. Methods of depositing said perfume onto fabric surfaces are disclosed.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

PERFUME DELIVERY SYSTEM COMPRISING ZEOLITES

5

FIELD OF THE INVENTION

The present invention relates to perfume delivery systems and methods of using said perfume delivery systems in detergent compositions, especially granular detergents.

BACKGROUND OF THE INVENTION

Most consumers have come to expect scented laundry products and to expect that fabrics which have been laundered also to have a pleasing fragrance. Perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carry-over from an aqueous laundry bath onto fabrics is often marginal. Industry, therefore, has long searched for an effective perfume delivery system for use in laundry products which provides long-lasting, storage-stable fragrance to the product, as well as fragrance to the laundered fabrics.

Laundry and other fabric care compositions which contain perfume mixed with or sprayed onto the compositions are well known from commercial practice. Because perfumes are made of a combination of volatile compounds, perfume can be continuously emitted from simple solutions and dry mixes to which the perfume has been added. Various techniques have been developed to hinder or delay the release of perfume from compositions so that they will remain aesthetically pleasing for a longer length of time. To date, however, few of the methods deliver significant fabric odor benefits after prolonged storage of the product.

Moreover, there has been a continuing search for methods and compositions which will effectively and efficiently deliver perfume from a laundry bath onto fabric surfaces. As can be seen from the following disclosures, various methods of perfume delivery have been developed involving protection of the perfume through the wash

- 2 -

cycle, with release of the perfume onto fabrics. U.S. Pat. 4,096,072, Brock et al, issued June 20, 1978, teaches a method for delivering fabric conditioning agents, including perfume, through the wash and dry cycle via a fatty quarternary ammonium salt. U.S. Pat. 4,402,856, Schnoring et al, issued Sept. 6, 1983, teaches a microencapsulation technique which involves the formulation of a shell material which will allow for diffusion of perfume out of the capsule only at certain temperatures. U.S. Pat. 4,152,272, Young, issued May 1, 1979, teaches incorporating perfume into waxy particles to protect the perfume through storage in dry compositions and through the laundry process. The perfume assertedly diffuses through the wax on the fabric in the dryer. U.S. Pat. 5,066,419, Walley et al, issued Nov. 19, 1991, teaches perfume dispersed with a water-insoluble nonpolymeric carrier material and encapsulated in a protective shell by coating with a water-insoluble friable coating material. U.S. Pat. 5,094,761, Trinh et al, issued Mar. 10, 1992, teaches a perfume/cyclodextrin complex protected by clay which provides perfume benefits to at least partially wetted fabrics.

Another method for delivery of perfume in the wash cycle involves combining the perfume with an emulsifier and water-soluble polymer, forming the mixture into particles, and adding them to a laundry composition, as is described in U.S. Pat. 4,209,417, Whyte, issued June 24, 1980; U.S. Pat. 4,339,356, Whyte, issued July 13, 1982; and U.S. Pat. No. 3,576,760, Gould et al, issued April 27, 1971. However, even with the substantial work done by industry in this area, a need still exists for a simple, more efficient and effective perfume delivery system which can be mixed with laundry compositions to provide initial and lasting perfume benefits to fabrics which have been treated with the laundry product.

The perfume can also be adsorbed onto a porous carrier material, such as a polymeric material, as described in U.K. Pat. Pub. 2,066,839, Bares et al, published July 15, 1981. Perfumes have also been adsorbed onto a clay or zeolite material which is then admixed into particulate detergent compositions. Generally, the preferred zeolites have been Type A or 4A Zeolites with a nominal pore size of approximately 4 Angstrom units. It is now

believed that with Zeolite A or 4A, the perfume is adsorbed onto the zeolite surface with relatively little of the perfume actually absorbing into the zeolite pores. While the adsorption of perfume onto zeolite or polymeric carriers may perhaps provide some improvement over the addition of neat perfume admixed with detergent compositions, industry is still searching for improvements in the length of storage time of the laundry compositions without loss of perfume characteristics, in the intensity or amount of fragrance delivered to fabrics, and in the duration of the perfume scent on the treated fabric surfaces.

Another problem in providing perfumed products is the odor intensity associated with the products, especially high density granular detergent compositions. As the density and concentration of the detergent composition increase, the odor from the perfume components can become undesirably intense. A need therefore exists for a perfume delivery system which substantially releases the perfume odor during use but which does not provide an overly-intensive odor to the product, itself.

By the present invention it has now been discovered that certain zeolites with a nominal pore size of at least about 6 Angstroms effectively incorporate perfume into their pores. Without wishing to be limited by theory, it is believed that these zeolites provide a channel or cage-like structure in which the perfume molecules are trapped. Unfortunately, such perfumed zeolites are not sufficiently storage-stable for commercial use in granular fabric care products such as laundry detergents, particularly due to premature release of perfume upon moisture absorption. However, it has now also been discovered that the perfumed zeolite can then be matrixed with simple water-soluble, but perfume-insoluble, materials (such as sugars) which form a protective barrier entrapping and maintaining the perfume within the zeolite's pores. Thus, the perfume substantially remains in the matrix, even under humid conditions, without the need for expensive, complex coatings, encapsulations, or resin layers. It is also believed that since the perfume is incorporated into the relatively large zeolite pores, it has better perfume retention through the laundry process than other smaller pore size zeolites in which the perfume is predominately adsorbed on the zeolite

surface. Fabrics treated by such perfume delivery systems thus have higher scent intensity and remain scented for longer periods of time after laundering.

The present invention solves the long-standing need for a simple, effective, storage-stable perfume delivery system which provides odor benefits during and after the laundering process, but which has reduced product odor during storage of the composition. The present invention, after removal of the matrix in the wash, provides the additional, unexpected benefit of continued odor release when exposed to heat or humidity while being stored, dried or ironed.

BACKGROUND ART

U.S. Patent 4,539,135, Ramachandran et al, issued September 3, 1985, discloses particulate laundry compounds comprising a clay or zeolite material carrying perfume. U.S. Patent 4,713,193, Tai, issued December 15, 1987, discloses a free-flowing particulate detergent additive comprising a liquid or oily adjunct with a zeolite material. Japanese Patent HEI 4[1992]-218583, Nishishiro, published August 10, 1992, discloses controlled-release materials including perfumes plus zeolites. U.S. Patent 4,304,675, Corey et al, issued December 8, 1981, teaches a method and composition comprising zeolites for deodorizing articles.

SUMMARY OF THE INVENTION

The present invention relates to a perfume delivery composition in the form of particles comprising:

- a) from about 10% to about 90%, preferably from about 60% to about 80%, by weight, of a solid, water-insoluble, porous carrier which comprises a natural or synthetic zeolite having a nominal pore size of at least about 6 Angstroms;
- b) a perfume which is releasably incorporated in the pores of said zeolite carrier to provide a perfumed zeolite; and
- c) from about 10% to about 90%, preferably from about 20% to about 40%, by weight, of a matrix coated on said perfumed zeolite which comprises a water-soluble (wash removable) composition in which the perfume is substantially insoluble, comprising from 0% to about 80%, by weight, of at least one solid polyol containing more than 3 hydroxyl

moieties and from about 20% to about 100%, by weight, of a fluid diol or polyol in which the perfume is substantially insoluble and in which the solid polyol is substantially soluble.

5 The perfumed zeolite comprises from about 5% to about 30%, preferably from about 5% to about 20%, most preferably from about 7% to about 15%, by weight, of perfume and from about 70% to about 95%, preferably from about 80% to about 95%, most preferably from about 85% to about 93%, by weight, of zeolite. Preferred zeolites
10 have a nominal pore size of at least about 6, preferably at least about 7 Angstroms, and a particle size no larger than about 120 microns, most preferably no larger than 30 microns. Preferred zeolites are faujasite-type zeolites selected from the group consisting of Zeolite X, Zeolite Y, and mixtures thereof. Typical,
15 but non-limiting, examples of perfume ingredients employed in this invention include those selected from the group consisting of hexyl cinnamic aldehyde, benzyl benzoate, dihydromyrcenol, eugenol, heliotropin, coumarin, and mixtures thereof.

Preferred fluid diols and polyols used in the matrix are
20 selected from the group consisting of glycerol, ethylene glycol, and diglycerol. Preferred solid polyols used in the matrix are selected from the group consisting of glucose, sorbitol, maltose, glucamine, sucrose, polyvinyl alcohol, starch, alkyl polyglycoside, sorbitan fatty ester, polyhydroxy fatty acid amides con-
25 taining from about 1 to about 18, preferably from 1 to 12, most preferably from 1 to 8, carbon atoms in their fatty acid moieties, and mixtures thereof.

The perfume delivery particles are preferably in agglomerated form, said agglomerates being dissociable in water and having an
30 average size of from about 200 microns to about 1000 microns, preferably from about 400 microns to about 600 microns. The agglomerated particles allow for admixing with detergent ingredients which have similar particle size.

35 The perfume delivery compositions herein can also be used in conventional detergent compositions, particularly in granular detergent compositions. The detergent composition will comprise from about 1% to about 20%, preferably from about 1% to about 8%, by weight, of said perfume delivery composition. The conventional

detergent ingredients employed in fully-formulated detergent compositions provided herein can comprise from about 1% to about 99%, preferably from about 5% to about 80% of a deterative surfactant. Optionally, detergent compositions can comprise from about 5% to about 80% of a deterative builder. Other optional detergent ingredients can also be included in the fully-formulated detergent/perfume compositions provided by this invention. A second perfume can be sprayed onto the surface of said detergent granules, thereby providing fragrance to the product while it is stored.

The perfume delivery system of this invention is particularly effective in high density granular detergent compositions. Such concentrated granular detergent compositions typically have a bulk density of at least 550 grams/liter, preferably at least about 650 grams/liter, and ranging as high as about 900 grams/liter.

The method for depositing perfume on fabrics comprises contacting fabrics with an aqueous liquor containing at least about 1 ppm of said perfume delivery composition and, optionally, at least about 100 ppm of conventional deterative ingredients. Preferably, the aqueous liquor contains from about 10 ppm to about 200 ppm, most preferably from about 10 ppm to about 80 ppm, of the perfume delivery composition. The invention also encompasses a method for providing odor benefits on fabrics during storage, drying, or ironing comprising contacting fabrics with an aqueous liquor containing at least about 1 ppm, preferably from about 10 ppm to about 200 ppm, most preferably from about 10 ppm to about 80 ppm, of said perfume delivery composition and, optionally, at least about 100 ppm of conventional deterative ingredients, and drying the fabric in an automatic dryer, applying heat to fabrics which have been line-dried or machine dried at low heat by conventional ironing means (preferably with steam or pre-wet), or storing fabrics which have been line-dried or machine dried at low heat under ambient conditions with humidity (above about 20%).

The perfume delivery composition can be prepared in an anhydrous system by a process which comprises the steps of:

- a) forming a perfumed zeolite by mixing porous, substantially dehydrated (less than 10%, preferably less than 5%,

water) Zeolite X or Y with a perfume such that the perfume is incorporated into the pores of the zeolite;

- b) forming a matrix by mixing a solid polyol containing more than 3 hydroxyl moieties with a fluid polyol or diol such as glycerol, ethylene glycol, or diglycerol to form a liquid; and
- c) mixing the matrix (b) with the perfumed zeolite (a) until free flowing particles are formed.

All percentages, ratios, and proportions herein are on a weight basis unless otherwise indicated. All documents cited are hereby incorporated by reference.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a perfume delivery system comprising a dehydrated zeolite, preferably Type X Zeolite, Type Y Zeolite, or a mixture thereof, wherein a perfume or a mixture of perfume and perfume fixative has been releasably absorbed in the pores of said zeolite. The perfumed zeolite is incorporated, in the absence of water, with a matrix preferably comprising a fluid diol or polyol and a solid polyol. The perfume delivery system is especially useful in granular detergent compositions.

The component materials are described below.

Perfume

As used herein the term "perfume" is used to indicate any pleasant smelling, odoriferous material which can be absorbed into the pores of the zeolites herein and which is subsequently released into the aqueous bath and/or onto fabrics contacted therewith. The perfume selected should be immiscible with the matrix materials employed in the perfume delivery system so as to limit loss of the perfume before use. The perfume will most often be liquid at ambient temperatures. A wide variety of chemicals are known for perfume uses, including materials such as aldehydes, ketones and esters. More commonly, naturally occurring plant and animal oils and exudates comprising complex mixtures of various chemical components are known for use as perfumes. The perfumes herein can be relatively simple in their compositions or can comprise highly sophisticated complex mixtures of natural and synthetic chemical components, all chosen to provide any desired odor. Typical perfumes can comprise, for example, woody/earthy bases containing

exotic materials such as sandalwood, civet and patchouli oil. The perfumes can be of a light floral fragrance, e.g., rose extract, violet extract, and lilac. The perfumes can also be formulated to provide desirable fruity odors, e.g., lime, lemon, and orange. Any
5 chemically compatible material which exudes a pleasant or otherwise desirable odor can be used in the perfumed compositions herein.

Examples of perfume ingredients deliverable by this invention include: hexyl cinnamic aldehyde, benzyl benzoate, dihydromyrcenol, eugenol, heliotropin, coumarin, and mixtures thereof.

10 Perfume Fixative

Optionally, the perfume can be combined with a perfume fixative. The perfume fixative materials employed herein are characterized by several criteria which make them especially suitable in the practice of this invention. Dispersible, toxicologically-acceptable,
15 able, non-skin irritating, inert to the perfume, degradable and/or available from renewable resources, and relatively odorless additives are used. Perfume fixatives are believed to slow the evaporation of more volatile components of the perfume.

Examples of suitable fixatives include members selected from
20 the group consisting of diethyl phthalate, musks, and mixtures thereof. If used, the perfume fixative comprises from about 10% to about 50%, preferably from about 20% to about 40%, by weight, of the perfume.

Zeolites

25 The term "zeolite" used herein refers to a crystalline aluminosilicate material. The structural formula of a zeolite is based on the crystal unit cell, the smallest unit of structure represented by



30 where n is the valence of the cation M, x is the number of water molecules per unit cell, m and y are the total number of tetrahedra per unit cell, and y/m is 1 to 100. Most preferably, y/m is 1 to 5. The cation M can be Group IA and Group IIA elements, such as sodium, potassium, magnesium, and calcium.

35 In general, the zeolite material useful in the present invention encompasses water-insoluble aluminosilicate particles with high adsorption efficiency, and a nominal pore size of at least about 6 Angstroms which is larger than the transverse axial

dimension of the perfume and optional perfume fixative molecules that are to be absorbed in the porous material but which is capable of retaining the perfume in the zeolite structure while being stored. Pore volumes and pore size distributions may be measured
5 by the recognized techniques of adsorption of sorbates of progressively increasing molecular diameter and by x-ray crystallography.

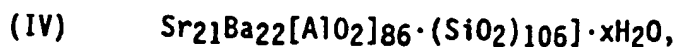
Contrary to the teachings of previous references, such as U.S. Pat. 4,304,675, and U.S. Pat. 4,539,135, both cited above, the use
10 of Zeolite A or 4A is believed to have pore sizes too small (4 Angstroms or less) for effective absorption of the perfume molecules. Thus, it is believed that the perfume incorporated on type A or 4A Zeolites will rapidly dissipate from the zeolites during wash. Hence, compositions comprising such zeolites are not
15 acceptable for effective carry-over of the perfume onto the fabrics which have been treated with them.

The preferred zeolite useful herein is a faujasite-type zeolite, including Type X Zeolite or Type Y Zeolite, both with a nominal pore size of about 8 Angstrom units, typically in the range
20 of from about 7.4 to about 10 Angstrom units.

The aluminosilicate zeolite materials useful in the practice of this invention are commercially available. The zeolites useful in this invention can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically
25 derived. Methods for producing X and Y-type zeolites are well-known and available in standard texts. Preferred synthetic crystalline aluminosilicate materials useful herein are available under the designation Type X or Type Y.

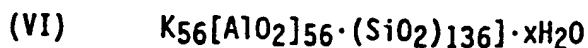
For purposes of illustration and not by way of limitation, in
30 a preferred embodiment, the crystalline aluminosilicate material is Type X and is selected from the following:

- (I) $\text{Na}_{86}[\text{AlO}_2]_{86} \cdot (\text{SiO}_2)_{106} \cdot x\text{H}_2\text{O}$,
- 35 (II) $\text{K}_{86}[\text{AlO}_2]_{86} \cdot (\text{SiO}_2)_{106} \cdot x\text{H}_2\text{O}$,
- (III) $\text{Ca}_{40}\text{Na}_6[\text{AlO}_2]_{86} \cdot (\text{SiO}_2)_{106} \cdot x\text{H}_2\text{O}$,



and mixtures thereof, wherein x is from about 0 to about 276. Zeolites of Formula (I) and (II) have a nominal pore size or opening of 8.4 Angstroms units. Zeolites of Formula (III) and (IV) have a nominal pore size or opening of 8.0 Angstroms units.

In another preferred embodiment, the crystalline aluminosilicate material is Type Y and is selected from the following:



and mixture thereof, wherein x is from about 0 to about 276. Zeolites of Formula (V) and (VI) have a nominal pore size or opening of 8.0 Angstroms units.

Zeolites used in the present invention are in particle form having an average particle size from about 0.5 microns to about 120 microns, preferably from about 0.5 microns to about 30 microns, as measured by standard particle size analysis technique.

The size of the zeolite particles allows them to be entrained in the fabrics with which they come in contact. Once established on the fabric surface (with their coating matrix having been washed away during the laundry process), the zeolites can begin to release their perfume, especially when subjected to heat or humid conditions.

Incorporation of Perfume in Zeolite - Type X or Type Y Zeolites are first activated/dehydrated by heating to about 150-350°C, optionally with reduced pressure (from about 0.001 to about 20 Torr), for at least 12 hours. After activation, the perfume is slowly and thoroughly mixed with the activated zeolite and, optionally, heated to about 60°C for about 2 hours to accelerate absorption equilibrium within the zeolite particles. The perfume/zeolite mixture is then cooled to room temperature and is in the form of a free-flowing powder.

Matrix

The matrix employed in the perfume delivery system of this invention comprises a fluid diol or polyol, such as glycerol,

- 11 -

ethylene glycol, or diglycerol (suitable fluid diols and polyols typically have a M.P. below about -10°C) and, optionally but preferably, a solid polyol containing more than three hydroxyl moieties, such as glucose, sorbitol, and other sugars. The solid polyol should be dissolvable with heating in the fluid diol or polyol to form a viscous (approximately 4000 cPs), fluid matrix (i.e., the consistency of honey). The matrix, which is insoluble with the perfume, is thoroughly mixed with the perfumed zeolite and, thereby, entraps and "protects" the perfume in the zeolite. Solubility of the matrix in water enables the perfumed zeolite to be released in the aqueous bath during laundering.

The preferred properties of the matrix formed by the fluid diol or polyol and the solid polyol include strong hydrogen-bonding which enables the matrix to attach to the zeolite at the siloxide sites and to compete with water for access to the zeolite; incompatibility of the matrix with the perfume which enables the matrix to contain the perfume molecules inside the zeolite cage and to inhibit diffusion of the perfume out through the matrix during dry storage; hydrophilicity of the matrix to enable the matrix materials to dissolve in water for subsequent perfume release from the zeolites; and humectancy which enables the matrix to serve as a limited water sink to further protect the perfumed zeolite from humidity during storage.

The matrix material comprises from about 20% to about 100%, preferably from about 50% to about 70%, by weight of the fluid diol or polyol and from 0% to about 80%, preferably from about 30% to about 50%, by weight, of one or more solid polyols. Of course, the proportions can vary, depending on the particular solid polyols and fluid polyols that are chosen. The perfume delivery system comprises from about 10% to about 90%, preferably from about 20% to about 40%, by weight of the diol/polyol matrix material, the balance comprising the perfume-plus-zeolite.

In addition to its function of containing/protecting the perfume in the zeolite particles, the matrix material also conveniently serves to agglomerate multiple perfumed zeolite particles into agglomerates having an overall particles size in the range of 200 to 1000 microns, preferably 400 to 600 microns. This reduces dustiness. Moreover, it lessens the tendency of the smaller,

individual perfumed zeolites to sift to the bottom of containers filled with granular detergents, which, themselves, typically have particle sizes in the range of 200 to 1000 microns.

The following nonlimiting example describes a typical laboratory preparation of the perfume delivery composition.

EXAMPLE I

About 119 g of Zeolite 13X powder is activated/dehydrated at 200°C at 14 Torr for about 24 hours. The activated zeolite (119 g) is added to a glass vessel, and 21 g of perfume (any commercial perfume is useful; Alba-C is typical) is slowly added with thorough mixing and shaking to yield an 85/15 zeolite:perfume ratio. The zeolite/perfume mixture is transferred to a mixer (Cuisinart) and mixed for approximately 20 seconds. The mixture is then returned to a glass vessel. The vessel is sealed and vibrated to compact the sample. The zeolite/perfume mixture is heated in the closed vessel at 60°C for 2 hours, and then cooled to room temperature.

In another glass vessel, 34.3g of anhydrous glycerol is heated to approximately 110-120°C with continuous stirring. To the glycerol is added 25.7g of anhydrous glucose to yield a 42.5:57.5 ratio of glycerol to glucose. Heating and stirring are continued until a clear, liquid solution is formed. The solution is cooled to room temperature.

To a large, flat crystallizing dish, first add the 60g of glycerol/glucose solution, and then add the 140g of zeolite/perfume. The solid zeolite/perfume is thoroughly mixed with the viscous liquid solution and transferred to a Cuisinart mixer for approximately 3 minutes of agitation. The resulting product, which is in the form of a free-flowing powder agglomerate, is then transferred to a container and sealed for storage.

The perfume delivery compositions are used in compositions with deterative ingredients, as follows.

Conventional Deterative Ingredients

Deterative Surfactant

The amount of deterative surfactant included in the conventional detergent ingredients employed in the present invention can vary from about 1% to about 99% by weight of the detergent composition depending upon the particular surfactant(s) used and the effects desired. Preferably, the deterative surfac-

tant(s) comprises from about 5% to about 80% by weight of the composition.

The deterative surfactant can be nonionic, anionic, ampholytic, zwitterionic, or cationic. Mixtures of these surfac- tants can
 5 also be used. Preferred detergent compositions, therefore, comprise anionic deterative surfactants or mixtures of anionic surfactants with other surfactants disclosed herein.

Nonlimiting examples of surfactants useful herein include the conventional C₁₁-C₁₈ alkyl benzene sulfonates and primary,
 10 secondary, and random alkyl sulfates, the C₁₀-C₁₈ alkyl alkoxy sulfates, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, C₁₂-C₁₈ alpha-sulfonated fatty acid esters, C₁₂-C₁₈ alkyl and alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and
 15 sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

One particular class of adjunct nonionic surfactants especially useful herein comprises the polyhydroxy fatty acid amides of the formula:



wherein: R¹ is H, C₁-C₈ hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl, most preferably C₁ alkyl (i.e., methyl); and
 25 R² is a C₅-C₃₂ hydrocarbyl moiety, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₉ alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of
 30 glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl moiety.
 35 Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the

individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH, -CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)₂(CHOR')-(CHOH)-CH₂OH, where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly -CH₂-(CHOH)₄-CH₂OH.

10 In surfactant formula (I), R¹ can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-isobutyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. For highest sudsing, R¹ is preferably methyl or hydroxyalkyl. If lower sudsing is desired, R¹ is preferably C₂-C₈ alkyl, especially n-propyl, iso-propyl, n-butyl, 15 iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

R²-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc. (It is to be understood that separate portions of the poly- hydroxy fatty acid amides can be used both as the deterative surfactant in 20 the detergent compositions herein, and as the solid polyol of the matrix material used to coat the preferred zeolites.)

Deterative Builders

Other conventional deterative ingredients optionally employed in the present invention include inorganic and/or organic deterative 25 sive builders to assist in mineral hardness control. Typically, these builders will comprise from about 5% to about 80% by weight of the detergent compositions.

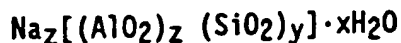
Inorganic deterative builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and 30 glassy polymeric meta-phosphates), phosphonates, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales.

35 Examples of silicate builders are the alkali metal silicates, particularly those having a SiO₂:Na₂O ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates

described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck.

5 Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Preferred aluminosilicates are zeolite builders which have the formula:



10 wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264. Such builders are Type A or 4A Zeolites, as distinguished from the Type X or Type Y Zeolites used to carry the perfume.

15 Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669; Krummel,
20 et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A and Zeolite P (B). Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

25 Organic deterative builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds, such as ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent
30 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987.

Other useful detergency builders include the ether hydroxy-polycarboxylates, copolymers of maleic anhydride with ethylene or
35 vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid,

oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders that can
5 also be used in detergent compositions, especially in combination with zeolite and/or layered silicate builders.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued
10 January 28, 1986.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium
15 orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Optional Detergent Adjuncts

20 As a preferred embodiment, the conventional detergent ingredients employed herein can be selected from typical detergent composition components such as detergent surfactants and detergent builders. Optionally, the detergent ingredients can include one or more other detergent adjuncts or other materials for assisting or
25 enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. Usual detergent adjuncts of detergent compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al. Such adjuncts which can be included in detergent compositions
30 employed in the present invention, in their conventional art-established levels for use (generally from 0% to about 80% of the detergent ingredients, preferably from about 0.5% to about 20%), include color speckles, suds boosters, suds suppressors, anti-tarnish and/or anticorrosion agents, soil-suspending agents, soil
35 release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, enzymes, enzyme stabilizing agents, solvents, solubilizing agents, chelating agents, clay soil removal/anti-redeposition agents, polymeric

dispersing agents, processing aids, fabric softening components, static control agents, bleaching agents, bleaching activators, bleach stabilizers, etc.

High Density Granular Detergent Composition

5 The perfume delivery composition can be used in both low density (below 550 grams/liter) and high density granular detergent compositions in which the density of the granule is at least 550 grams/liter. Such high density detergent compositions typically comprise from about 30% to about 90% of deterative surfactant.

10 Low density compositions can be prepared by standard spray-drying processes. Various means and equipment are available to prepare high density granular detergent compositions. Current commercial practice in the field employs spray-drying towers to manufacture granular laundry detergents which often have a density
15 less than about 500 g/l. Accordingly, if spray drying is used as part of the overall process, the resulting spray-dried detergent particles must be further densified using the means and equipment described hereinafter. In the alternative, the formulator can eliminate spray-drying by using mixing, densifying and granulating
20 equipment that is commercially available. The following is a nonlimiting description of such equipment suitable for use herein.

High speed mixer/densifiers can be used in the present process. For example, the device marketed under the trademark "Lodige CB30" Recycler comprises a static cylindrical mixing drum
25 having a central rotating shaft with mixing/cutting blades mounted thereon. Other such apparatus includes the devices marketed under the trademark "Shugi Granulator" and under the trademark "Drais K-TTP 80". Equipment such as that marketed under the trademark "Lodige KM600 Mixer" can be used for further densification.

30 In one mode of operation, the compositions are prepared and densified by passage through two mixer and densifier machines operating in sequence. Thus, the desired compositional ingredients can be admixed and passed through a Lodige mixture using residence times of 0.1 to 1.0 minute then passed through a second
35 Lodige mixer using residence times of 1 minute to 5 minutes.

In another mode, an aqueous slurry comprising the desired formulation ingredients is sprayed into a fluidized bed of particulate surfactants. The resulting particles can be further

densified by passage through a Lodige apparatus, as noted above. The perfume delivery particles are admixed with the detergent composition in the Lodige apparatus.

The final density of the particles herein can be measured by
5 a variety of simple techniques, which typically involve dispensing a quantity of the granular detergent into a container of known volume, measuring the weight of detergent and reporting the density in grams/liter.

Once the low or high density granular detergent "base"
10 composition is prepared, the agglomerated perfume delivery system of this invention is added thereto by any suitable dry-mixing operation.

Deposition of Perfume onto Fabric Surfaces

The method of washing fabrics and depositing perfume thereto
15 comprises contacting said fabrics with an aqueous wash liquor comprising at least about 100 ppm of conventional deterative ingredients described hereinabove, as well as at least about 1 ppm of the above-disclosed perfume delivery system. Preferably, said aqueous liquor comprises from about 500 ppm to about 20,000 ppm of
20 the conventional deterative ingredients and from about 10 ppm to about 200 ppm of the perfume delivery system.

The perfume delivery system works under all circumstances, but is particularly useful for providing odor benefits on fabrics during storage, drying or ironing. The method comprises con-
25 tacting fabrics with an aqueous liquor containing at least about 100 ppm of conventional deterative ingredients and at least about 1 ppm of the perfume delivery composition such that the perfumed zeolite particles are entrained on the fabrics, storing line-dried fabrics under ambient conditions with humidity of at least 20%,
30 drying the fabric in a conventional automatic dryer, or applying heat to fabrics which have been line-dried or machine dried at low heat (less than about 50°C) by conventional ironing means (preferably with steam or pre-wetting).

The following nonlimiting examples illustrate the parameters
35 of and compositions employed within the invention. All percentages, parts and ratios are by weight unless otherwise indicated.

EXAMPLE II

A granular detergent composition is prepared comprising the following ingredients.

	<u>Component</u>	<u>Weight %</u>
5	C ₁₂ linear alkyl benzene sulfonate	22
	Phosphate (as sodium tripolyphosphate)	30
	Sodium carbonate	14
	Sodium silicate	3
	Sodium percarbonate	5
10	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Sodium sulfate	5.5
	Perfume Delivery System (Example I)	3.0
	Nonanoyloxybenzenesulfonate	5
	Minors, filler* and water	Balance to 100%

15 *Can be selected from convenient materials such as CaCO₃, talc, clay, silicates, and the like.

An aqueous crutcher mix of heat and alkali stable components of the detergent composition is prepared and spray-dried. The other ingredients, including the perfume delivery system, are
20 admixed in the final composition so that the composition contains the ingredients tabulated at the levels shown.

The detergent granules are added together with 5 lb. (2.3 kg) of previously laundered fabrics to an automatic washing machine to provide a detergent concentration of 1000 ppm in the 17 gallon (65
25 l) water-fill machine. Fabrics laundered with the composition and dried have a noticeable perfume fragrance. The fragrance intensity is still unchanged approximately 6 days after drying of the fabrics at 60-70°C for 40 minutes.

EXAMPLE III

30 A granular detergent composition is prepared comprising the following ingredients.

	<u>Component</u>	<u>Weight %</u>
	Anionic alkyl sulfate	7
	Nonionic surfactant	5
35	Zeolite A (0.1-10 micron)	10
	Trisodium citrate	2
	SKS-6 silicate builder	10
	Acrylate maleate polymer	4

- 20 -

	Sodium carbonate	5
	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Perfume Delivery System (Example I)	4.0
	Suds suppressor	2
5	Enzymes*	1.5
	Soil release agent	0.2
	Minors, filler** and water	Balance to 100%

*1:1:1 mixture of protease, lipase, and cellulase.

**Can be selected from convenient materials such as CaCO₃, talc,
10 clay, silicates, and the like.

An aqueous crutcher mix of heat and alkali stable components of the detergent composition is prepared and spray-dried. The other ingredients, including the perfume delivery system, are admixed therewith so that the final composition contains the
15 ingredients tabulated at the levels shown.

The detergent granules are added via the dispensing drawer together with 5 lb. (2.3 kg) of previously laundered fabrics to an automatic washing machine. Actual weight of detergent composition is taken to provide an 8,000 ppm concentration in the 17 l water-
20 fill machine. Fabrics laundered with the composition and line-dried have a noticeable perfume fragrance after either ironing or storage.

EXAMPLE IV

A laundry bar comprises the following.

25	<u>Component</u>	<u>Weight %</u>
	C ₁₂ linear alkyl benzene sulfonate	30
	Phosphate (as sodium tripolyphosphate)	7
	Sodium carbonate	25
	Sodium pyrophosphate	7
30	Coconut monoethanolamide	2
	Zeolite A (0.1-10 micron)	5
	Carboxymethylcellulose	0.2
	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Polyacrylate (m.w. 1400)	0.2
35	Nonanoyloxybenzenesulfonate	5
	Sodium percarbonate*	5

- 21 -

	Brightener	0.2
	Perfume delivery system (Example I)	3.0
	Protease	0.3
	CaSO ₄	1
5	MgSO ₄	1
	Water	4
	Filler**	Balance to 100%

*Average particle size of 400 to 1200 microns.

**Can be selected from convenient materials such as CaCO₃, talc,
10 clay, silicates, and the like.

The detergent laundry bar is extruded in conventional soap or
detergent bar making equipment as commonly used in the art.
Testing is conducted following the testing methods in Example II.
Fabrics laundered with the composition and line-dried have a
15 noticeable perfume fragrance after ironing or storage.

EXAMPLE V

A high density granular detergent comprises the following.

	<u>Component</u>	<u>Weight %</u>
	C ₁₂₋₁₄ linear alkyl benzene sulfonate	15
20	Sodium citrate	5
	Sodium carbonate	20
	Zeolite A (0.1-10 micron)	26
	Brightener	0.1
	Perfume delivery system (Example I)	3.0
25	Detersive enzyme (1:1 LIPOLASE/ESPERASE)	1.0
	Sodium Sulphate	15
	Water and fillers**	Balance to 100%

**Can be selected from convenient materials such as CaCO₃, talc,
30 clay, silicates, and the like.

An aqueous crutcher mix of heat and alkali stable components
of the detergent composition is prepared and spray-dried. The
resulting granules are passed through a Lodige CB mixer until a
density of 650 grams/liter is secured. The other ingredients,
including the perfume delivery system, are admixed therewith so
35 that the final composition contains the ingredients tabulated at
the levels shown.

- 22 -

Testing is conducted following the testing methods in Example II. Fabrics laundered with the composition have a noticeable perfume fragrance after drying in an automatic dryer at 60-70°C for approximately 40 minutes.

5

10

15

20

25

30

35

What is Claimed is:

1. A perfume delivery composition in the form of particles comprising:
 - a) a solid, water-insoluble, porous carrier which comprises a natural or synthetic zeolite having a nominal pore size of at least 6 Angstroms;
 - b) a perfume which is releasably incorporated in the pores of said zeolite carrier to provide a perfumed zeolite; and
 - c) a matrix coated on said perfumed zeolite which comprises a water-soluble composition in which the perfume is substantially insoluble, comprising from 0% to 80%, by weight, of at least one solid polyol containing more than 3 hydroxyl moieties and from 20% to 100%, by weight, of a fluid diol or polyol in which the perfume is substantially insoluble and in which the solid polyol is substantially soluble.
2. A composition according to Claim 1 wherein said fluid polyol or diol is selected from the group consisting of glycerol, ethylene glycol, and diglycerol.
3. A composition according to either of Claims 1 or 2 wherein the solid polyol is selected from the group consisting of glucose, sorbitol, maltose, glucamine, sucrose, polyvinyl alcohol, starch, alkyl polyglycoside, sorbitan fatty ester, polyhydroxy fatty acid amides whose fatty acid moieties contain from 1 to 18 carbon atoms, and mixtures thereof.
4. A composition according to any of Claims 1-3 wherein the zeolite is Zeolite X or Zeolite Y.
5. A composition according to any of Claims 1-4 wherein the perfume is selected from the group consisting of hexyl cinnamic aldehyde, benzyl benzoate, dihydromyrcenol, eugenol, heliotropin, coumarin, and mixtures thereof.
6. A composition according to any of Claims 1-5 wherein the perfumed zeolite comprises from 5% to 30%, by weight, of the perfume.
7. A composition according to any of Claims 1-6 wherein the perfume further comprises a perfume fixative.

8. A granular detergent composition comprising:
 - a) from 5% to 80%, by weight, of a deterative surfactant; and
 - b) from 1% to 20%, by weight, of the perfume delivery composition according to any of Claims 1-7.
9. A detergent composition according to any of Claims 1-8 further comprising a second perfume sprayed onto the surface of said detergent granules.
10. A perfume delivery composition derived by a process which comprises the steps of:
 - (a) forming a perfumed zeolite by mixing porous, substantially dehydrated Zeolite X or Y with a perfume such that the perfume is incorporated into the pores of the zeolite;
 - (b) forming a matrix by mixing a solid polyol containing more than 3 hydroxyl moieties with glycerol, ethylene glycol, or diglycerol to form a liquid; and
 - (c) mixing the matrix (b) with the perfumed zeolite (a) until free flowing particles are formed.

INTERNATIONAL SEARCH REPORT

Internat'l Application No.

PCT/US 94/06050

A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C11D3/50 C11D3/12 A61K7/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C11D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 339 356 (D.D. WHYTE) 13 July 1982 cited in the application see column 4, line 20 - column 5, line 2 ---	1-3,6,8
A	EP,A,0 535 942 (UNILEVER) 7 April 1993 see page 2, line 43 - page 3, line 35; claims; example 1 ---	1,4-6
A	GB,A,2 140 820 (COLGATE-PALMOLIVE) 5 December 1984 cited in the application see claims ---	1
A	FR,A,2 546 904 (COLGATE-PALMOLIVE) 7 December 1984 see claims ---	1
	--- -/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

& document member of the same patent family

Date of the actual completion of the international search

17 October 1994

Date of mailing of the international search report

03.11.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Grittern, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 94/06050

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with location, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 8218, Derwent Publications Ltd., London, GB; Class A97, AN 82-36331E & JP,A,57 052 458 (DUSKIN FRANCHISE KK) 27 March 1982 see abstract</p> <p>-----</p>	1,5

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4339356	13-07-82	CA-A- 1175753 GB-A, B 2090278 JP-A- 57171910	09-10-84 07-07-82 22-10-82
EP-A-0535942	07-04-93	AU-A- 2616292 CA-A- 2079241 JP-A- 5209188	08-04-93 03-04-93 20-08-93
GB-A-2140820	05-12-84	US-A- 4536315 AT-B- 390078 AU-B- 562760 AU-A- 2879384 BE-A- 899804 CA-A- 1232548 CH-A- 660752 DE-A- 3419574 FR-A, B 2546903 LU-A- 85395 NL-A- 8401746 SE-C- 459974 SE-A- 8402867	20-08-85 12-03-90 18-06-87 06-12-84 03-12-84 09-02-88 15-06-87 06-12-84 07-12-84 26-03-85 02-01-85 21-12-89 02-12-84
FR-A-2546904	07-12-84	US-A- 4539135 AT-B- 390077 AU-B- 558639 AU-A- 2879284 BE-A- 899803 CA-A- 1235066 CH-A- 660601 DE-A- 3419561 GB-A, B 2141730 LU-A- 85394 NL-A- 8401745 SE-A- 8402872	03-09-85 12-03-90 05-02-87 06-12-84 03-12-84 12-04-88 15-05-87 06-12-84 03-01-85 26-03-85 02-01-85 02-12-84